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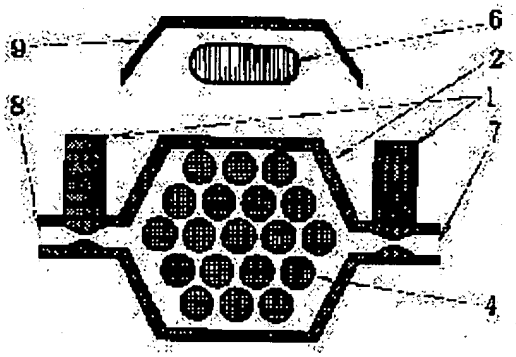
(54) MEASURING METHOD FOR COD

(57)Abstract:

PURPOSE: To dispense with a number of equipments and reagents and measure chemical oxygen demand (COD) in a short time by treating water containing dissolved oxygen with an optical catalyst under light irradiation, and detecting the dissolved oxygen concentration change before and after the treatment.

CONSTITUTION: A reacting vessel 2 is formed of a light permeable plastic material. Sample water is poured thereto from an injection hole 7, and the dissolved oxygen is determined by a dissolved oxygen detector 1. The sample water is treated by the contact with an optical catalyst 4 emitted from a light source 6. The dissolved oxygen concentration of the treated sample is determined by the detector 1. From the dissolved oxygen concentration change before and after the optical catalyst treatment, the oxygen consumption is calculated. In this optical catalytic reaction, the reduction reaction of oxygen is consumed as the reaction with a conductive charged electron. Therefore, the dissolved oxygen consumption in the optical catalytic reaction solution is substantially similar to COD. As the optical catalyst 4, TiO2, ZnO and those in which Pt, Ph are supported by these powders are used.



* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] Quantitative analysis of COD characterized by processing the water containing dissolved oxygen with the photocatalyst by which the optical exposure is carried out, and detecting the dissolved-oxygen-concentration change before and behind processing.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of measuring chemical oxygen demand (COD) used as the index of water quality managements, such as water quality management of various industrial wastewater, city sewage, pool water, a waterworks, a lake, the ocean, etc. and chemical process water, and ultrapure water.
[0002]
[Description of the Prior Art] The water quality monitor of various items is carried out to water quality management of various kinds of industrial wastewater, a waterworks, a lake, a river, the ocean, etc. Development of the exact and simple measuring method of an impurity included in underwater [these] is desired with development of the technique of removing the pollutant with which aggravation of the water quality accompanying contamination of a lake, a river, the ocean, etc. poses a problem, and becomes this cause from a rise of the consciousness of earth environmental protection especially in recent years. Although it dissolves or suspends and various impurities are contained in underwater [these] by the hysteresis of the water, the present condition is that performing a qualitative quantum about all matter needs a great effort difficult technically about the organic substance which is dissolving among these. Therefore, about these organic substance, chemical oxygen demand (COD), biological oxygen demand (BOD), or the amount (TOC) of total organic carbon is used according to the purpose as a standard of the total amount, and COD is used for water quality management of various fields especially as a water quality standard item which the Ministry of Health and Welfare defines.
[0003] Quantitative analysis of COD is performed by the oxidation reduction titrimetric method which uses potassium permanganate as an oxidizer and uses oxalic acid sodium as the reducing agent for back titrations as set to JIS-K -0102. That is, after making a sample underwater chlorine component react with a silver nitrate, the potassium permanganate of a constant rate is added, for example, oxidation actuation is performed for 30 minutes at 100 degrees C. Here, reducibility components, such as a sample underwater organic substance component, consume potassium permanganate while oxidizing. Next, by oxalic acid sodium and potassium permanganate, the back titration of this consumption of potassium permanganate is carried out, and it is computed as an oxygen demand.
[0004]
[Problem(s) to be Solved by the Invention] Since measurement of COD needs to prevent deterioration of sample water as much as possible, measuring immediately after extracting a sample is desirable. However, in order to perform measurement actuation, two kinds of oxidizers and the reducing-agent water solution which performed standardization correctly beforehand are needed not to mention a glass instrument required for oxidation reduction titration. And since the measurement actuation for every sample needed several times also at the lowest, it is difficult to measure on the spot which extracted sample water in fact, and it had the trouble that measurement also took a long time again.
[0005]
[Means for Solving the Problem] This invention processes the water containing dissolved oxygen with

the photocatalyst by which the optical exposure is carried out, by detecting the dissolved-oxygen-concentration change before and behind processing, tends to measure COD and tends to solve the problem like ****.

[0006]

[Function] The light of appropriate wavelength which has the energy more than the band gap to a semi-conductor is irradiated, and application of deordorization (JP,63-80833,A) of the water purification (JP,2-55117,B), manufacture (JP,62-193696,A) of ultrapure water, and the vehicle interior of a room, sterilization (JP,61-76160,A) of water, etc. is proposed. [photocatalyst / which promotes the oxidation reduction reaction of the solution kind with which the electronic-electron hole pair generated in the semi-conductor touches a semi-conductor / semi-conductor]

[0007] Although there are some descriptions in the reaction of this semi-conductor photocatalyst, the biggest description is having very strong oxidizing power. For example, it is known that, as for the titanium oxide which is excellent in chemical stability among various semi-conductors which can serve as a photocatalyst, the electron hole which draws out an electron from a solution kind has the potential energy of 3.0V (normal-hydrogen-electrode criteria) under the exposure of near-ultraviolet light. This is 1.23V of O2 / H2 O, and O3/O2. Even if it compares with 2.07V, there is capacity which also oxidizes remarkable refractory organic substances theoretically so that it may understand. Decomposition reactions, such as organic chlorine-based solvents (60 Hisanaga, Tanaka, electrochemistry, 2,107 (1992)), such as LAS known as a difficulty resolvability compound, PCB (53 Izumi, electrochemistry, 3,178 (1985)), and a trichloroethylene, are actually reported, respectively. When it is going to remove conversely the organic substance which is dissolving underwater, oxidative degradation of almost all the organic substance is carried out for this strong oxidizing power. Thus, it is thought that the description of being comparatively lacking in the selectivity of a reaction is also convenient to the above-mentioned application by which the conventional proposal is made.

[0008] Thus, although various application of the reaction of a semi-conductor photocatalyst is proposed, the reaction of these single strings is effectiveness acquired by the reaction of an electron hole which carried out optical generation. However, the reaction of a conduction band electron in which one side carried out optical generation did not not much have being used positively. Then, in many cases, this invention persons found out that the dissolved oxygen consumption of photocatalysis liquid was essentially similar to COD in these photocatalyses paying attention to the reduction reaction of oxygen being consumed as a reaction with a conduction band electron. Then, it resulted in this invention as a result of sincerity research. Then, the configuration of this invention is stated to a detail mainly based on Fig. 1 below.

[0009] First, if it is a means by which dissolved oxygen concentration is detectable, either can be used for the dissolved oxygen detector 1. Although what is necessary is just to choose according to constraint of the precision searched for, the magnitude of equipment, etc., electrochemistry type sensors, such as a galvanic cell type from the reasons of economical efficiency etc. and a polarograph type, are desirable in a speed of response and the ease of dealing with it. However, it is not limited to this. Moreover, it is the purpose of eliminating the effect of temperature which extends measuring range and which raises the accuracy of measurement, and when the dissolved oxygen concentration of sample water needs to be managed correctly, it is effective if a means by which sample water saturates oxygen and air beforehand is adopted.

[0010] Next, a reactor 2 consists of ingredients, such as plastics with translucency, such as glass, such as a quartz, a hoe silicic acid, and soda, or acrylic, and a vinyl chloride system. Or it is good also as a configuration which formed the light transmission aperture 3 which becomes ingredients, such as plastics, a metal, and a ceramic, from the above-mentioned translucency ingredient. Moreover, as for these ingredients, it is desirable for the elution of the organic substance to be few low ingredients of oxygen permeability in order to raise the accuracy of measurement. In a reactor, it exists in that a photocatalyst 4 is powdered, or a base material and the form fixed by the reactor itself. A reactor 2 is made into the configuration of a globular shape, cylindrical, a prismatic form, tubular, plate-like, discoid, or the shape of these hollow from conditions, such as effectiveness of the optical exposure by

the strength of the light source, the residence time of sample water, and pressure loss. When it is a cylinder-like hollow configuration, plate-like, or a tubing-like spiral configuration especially, there is an effective thing.

[0011] In a photocatalyst 4 TiO2, ZnO, SrTiO3, CdS, GaP and InP, GaAs, BaTiO3, K2 NbO, Fe 2O3, Ta 2O5, WO3, SnO2, Bi 2O3, NiO, Cu2 O, SiC and SiO2, MoS2, InPb, RuO2 and CeO2 etc. -- and the metallic-oxide photocatalyst which supported a metal and metallic oxides, such as Pt, Rh, RuO2, and Nb, Cu, Sn, NiO, to these photocatalyst powder -- All well-known things called molecule photocatalysts, such as a metal complex of bipyridyls, such as Mn, Zn, Mg, Ru, Fe, and Cu, or porphyrins, and these derivatives, can be conventionally adapted. Moreover, when the mediator of the reaction which promotes the reduction reaction of oxygen is added to these photocatalysts, there is an effective thing. Although it can take various configurations, such as the shape of the shape of powder and film, and porosity, when the effectiveness of optical pumping etc. is taken into consideration in separation with sample water, and the ease of dealing with it, the shape of film fixed on base materials, such as plastics, a ceramic, and glass, and the porous thing of a photocatalyst 4 are desirable. Moreover, when using a powder-like thing, it is desirable to use together the filter 5 for separating a photocatalyst.

[0012] Moreover, the source of the natural light of the light from artificial sources, such as fluorescent lamps, such as high-intensity-discharge LGTs, such as filament lamps, such as the light source, for example, an incandescent lamp, which can excite the photocatalyst to be used, and a halogen LGT, a mercury-vapor lamp, and a xenon LGT, a fluorescent lamp, the black light, and germicidal lamp glass, and the laser light source, or sunlight can be used for the light source 6. Moreover, an artificial source may be used for coincidence as a source of a fill-in flash of the solar light source. Moreover, it is also effective that introduce a reflecting plate 10 in any case, and it condenses.

[0013] Then, in drawing 1 , sample water is first poured in from the measured water inlet 7, and the quantum of dissolved oxygen concentration is made by the dissolved oxygen detector 1. Next, contact processing of the sample water is carried out with the photocatalyst 4 by which the optical exposure is carried out from the light source 6 in the reactor. The quantum of the sample water processed by the photocatalyst is carried out in the dissolved oxygen concentration after photocatalyst processing by the dissolved oxygen detector 1. Then, an oxygen demand is calculated from the dissolved-oxygen-concentration change before and behind photocatalyst processing. actuation of these single strings -- a batch method and a continuous method -- any are sufficient. Moreover, one dissolved oxygen detector can be good, the measured water inlet 7 can be used as an entrance, a dissolved oxygen detector can be arranged in the method and reactor which do not form the measurement water exhaust port 8, after introducing sample water, an optical exposure can be performed, and the effectiveness that the method which detects dissolved-oxygen-concentration change serially is the same can be acquired.

[0014] Now, this invention persons came to get completely different quantitative analysis of COD from the conventional COD measurement which is simple and can measure COD correctly and very quickly by taking the configuration explained in full detail above. It is thought that an operation of this invention is fundamentally accompanied by the following reaction mechanisms. That is, in the system which contains water like this invention in large quantities, the electron hole of the electronic-electron hole pair in the photocatalyst by which optical pumping was carried out oxidizes the water or the surface water acid radical near the photocatalyst front face, and generates a hydroxy radical. Next, this hydroxy radical oxidizes the sample underwater reducibility matter.

[0015]

[Formula 1]

$$\left.\begin{array}{l} OH + h^{+} \longrightarrow \dot{O}H \\ \dot{O}H + R_{Red} \longrightarrow R_{ox} \end{array}\right.$$

[0016] The reaction of one electron returns sample underwater molecular oxygen, generates a superoxide anion, and consumes oxygen.
[0017]
[Formula 2]

$$O_2 + e^- \longrightarrow O_2^-$$

[0018] However, when the sample underwater reducibility matter is lost, for example, as for consumption of molecular oxygen stopping seemingly, why etc. and the mechanisms of action also have many still unknown points, and it serves as a future research technical problem.
[0019]
[Example] Hereafter, this invention is explained using a suitable example.
[Example 1] The water which dissolved 5 ppm ethanol in the ion exchange and the water distilled and refined, and the water which diluted this 2, 5, 10, and 20 or 50,100 times were first used for sample water. It asked by the approach to which the consumption of potassium permanganate [in / for this / 100 degrees C] is first set in JIS-K -0102.
[0020] Next, system of measurement as shown in drawing 2 was used for the system of measurement which carries out this invention. Here, the reactor 2 wound 3m of bore hard-glass tubing of 3mm around the spiral configuration with a diameter of 10cm, and used the galvanic cell type oxygen sensor by Japan Storage Battery Co., Ltd. for the dissolved oxygen detector 1. The titanium oxide of a sol gel process which hydrolyze titanium tetraisopropoxide within a reactor and the titanium oxide sol was made to adhere to a wall, was crystallized while calcinating and fixing at 400 degrees C, and was obtained was used for the photocatalyst 4. It installed into the spiral of a reactor at the light source 6 using 2kW high-pressure mercury lamp.
[0021] Then, performing the optical exposure from a high-pressure mercury lamp, sample water was introduced from the measured water inlet 7 by the 1l. rate of flow for 1 minute, and the dissolved-oxygen-concentration change before and behind processing was detected. When this was compared with the oxygen demand beforehand calculated by the approach given in JIS, the very good correlation was acquired (drawing 4).
[0022] River water was used for [example 2] sample water, and it experimented on system of measurement using the system as shown at drawing 3 . What installed the galvanic cell type dissolved oxygen sensor 1 used in the example 1 in the side face on the cylinder with a diameter [made from quartz glass / of 50mm] and a height of 90mm was used for the reactor 2. P-25,110mg of titanium oxide made from Japanese Aerosil was suspended and used for the photocatalyst 4 sample underwater. Sample water was always between measurement agitated with the magnetic stirrer beforehand arranged in a reactor 2. Using 1kW metal halide lamp, the optical exposure for 30 minutes was performed, after optical exposure initiation, the oxygen density which dissolved oxygen concentration decreased and became constant value was detected in the light source 6, and it was asked for the oxygen demand. When compared with the oxygen demand which asked for this by the approach given in JIS, the very good correlation was acquired.
[0023]
[Effect of the Invention] As stated above, this invention processes the water containing dissolved oxygen with the photocatalyst by which the optical exposure is carried out, and relates to the quantitative analysis of COD characterized by detecting the dissolved-oxygen-concentration change before and behind processing. According to this invention, the big effectiveness it not only does not need the instrument for analysis, or two kinds of the oxidizers and the reducing agents which were needed conventionally, but that measurement is possible in an extraordinary short time compared with the former is acquired. Worth of this invention is large.

[Translation done.]